

Co/K_xTi₂O₅ catalysts prepared by ion exchange method for NO oxidation to NO₂

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Abstract

Co/K_xTi₂O₅ catalysts prepared by ion exchange method were tested for NO oxidation to NO₂. Their catalytic activities are similar to Pt-based catalysts and much higher than Co impregnated on TiO₂ with or without doped K. The conversion pattern shows a typical kinetic control at low temperatures and thermodynamic control at higher temperatures, exhibiting a peak temperature at which the conversion becomes a maximum. Conversion decreases sharply as oxygen concentration decreases below 1.0%. NO concentration shows a positive effect on the conversion. The presence of Co₃O₄ and K ion remaining in K_xTi₂O₅ after the ion exchange is responsible for the observed catalytic activity. Thus, Co/K_xTi₂O₅ having a complete ion exchange with little K is not active for the reaction. Unlike Pt-based catalyst, the presence of NO₂ does not inhibit catalytic activity. Co/K_xTi₂O₅ was resistant to the presence of SO₂ less than 10 ppm. High-NO oxidation activity and high resistance to SO₂ and NO₂ make Co/K_xTi₂O₅ a promising catalyst for NO oxidation.

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1. Introduction

Lean burn engines, of which diesel engine is a common example, are generally more fuel-efficient than stoichiometric engines, thereby giving a longer traveling distance per unit of fuel and, consequently, reduced CO₂ emission [1]. However, emission standards of diesel engines are becoming more and more severe. In 2005, for example, soot and NO_x productions were limited to 25 mg km⁻¹ and 250 mg km⁻¹, respectively, according to Euro IV regulations, twice as low as Euro III standards [2]. In order to meet NO_x emission levels, three approaches can be used: NO_x storage and reduction (NSR), selective catalytic reduction (SCR) and continuously regenerating trap (CRT) [3–8].

For adopting these technologies, it becomes evident now that NO₂ plays a decisive role [9,10]. For the NO_x storage and reduction (NSR), NO is first oxidized to NO₂ on platinum and then stored on BaO as nitrate [11]. For selective catalytic

reduction (SCR) technology, it has been proved that SCR reaction rate can be substantially increased, when a fraction of NO in the exhaust is converted to NO₂. This effect is more pronounced at lower temperatures (200–300 °C) when the reaction mixture contains equimolar amounts of NO and NO₂ (fast SCR process) [12–14]. For continuously regenerating trap (CRT), NO₂ is used as a strong oxidizer to oxidize soot collected on a particulate filter at comparably low temperatures. These temperatures are much lower than the ignition temperature of soot in air, which is typically around 550 °C.

However, nitrogen oxides (NO + NO₂) produced by combustion engines consist mainly of NO. Thus, the oxidation of NO to NO₂ is an important step for the after treatment reactions. At present, it is mainly achieved by using Pt-based catalyst or plasma. Pt-based catalysts have been comprehensively studied by many authors in the area of oxidation efficiency with NO and O₂; influence of Pt particle size; effects of precursors and support, SO₂, water and CO [14,15,17–23]. Kinetic modeling and simulations have also been carried out. For commercial application of Pt-based catalysts, however, many problems remain to be solved [2,16,24,25]. Pt has shown a decrease of activity when it was exposed to NO + O₂ at 250 °C [2,19,26]. This deactivation was attributed, according to

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XPS data, to the oxidation of Pt to PtO or PtO₂, which are less active than reduced platinum. Pt-based catalyst also oxidizes SO₂ to SO₃, which then forms sulfate with support alumina (such as Al₂(SO₄)₃), leading to a decrease in the catalytic activity [2,17,21,33]. Mulla et al. [22] have reported that the presence of water vapor in the feed results in an irreversible decrease in the active Pt surface area and a corresponding loss of NO conversion, for both Pt-K/Al₂O₃ and Pt/Al₂O₃ catalysts. The blocking of the Pt sites caused possibly by the migration of impurities from the support is believed to be the reason of the water poisoning. Zhu et al. [27] have also concluded that silica is not a good support when water is present although silica has been found to be better than alumina in the absence of water.

There has been little attempt to search substitute for Pt-based catalyst. Kantcheva et al. [28,29] have reported that Co³⁺ ions are able to oxidize NO to NO²⁺ and NO³⁺ species at room temperature, which could be a promising substitute for Pt-based catalyst. Mulla et al. [22] observed a lower apparent activation energy for Pt/K/Al₂O₃ catalyst (60 kJ mol⁻¹) compared to Pt/Al₂O₃ catalyst (82 kJ mol⁻¹). The turnover rate was also higher on Pt/K/Al₂O₃ catalyst. This promotional effect of K on Pt was by a factor of about 2 at 300 °C. They attributed it to the enhancement of O₂ absorption on Pt/K/Al₂O₃ surface.

It is widely accepted that TiO₂ is more resistant to SO_x. Therefore, a catalyst composing of Co, K and TiO₂ might have a potential for NO oxidation to NO₂ and low SO_x poisoning. Recently it has been found that K₂Ti₂O₅ exhibits the highest catalytic activity and photoluminescence compared with other layered titanates [30]. The present study reports a new catalyst of Co/K_xTi₂O₅ as alternative of Pt-based catalysts. Study includes preparation and characterization of the catalysts and activity comparison with Pt-based catalysts for the NO oxidation. The reaction was investigated by varying concentration of oxygen, nitrogen oxide and GHSV. The active species and the promotion effect of support for NO oxidation were also studied. Deactivation of the catalysts in the presence SO₂ and NO₂ was also evaluated.

2. Experimental

2.1. Catalyst synthesis

The flow chart of the synthesis of Co/K_xTi₂O₅ catalysts is outlined in Fig. 1. K₂Ti₂O₅ was first prepared by solid-state reaction. Potassium carbonate (Yakuri Pure Chemical Co., Ltd.) and titanium dioxide (Hombikat UV 100) were mixed together with a proper amount of water (molar ratio of K₂CO₃:TiO₂:H₂O = 1:2:15), and subjected to ball milling for 24 h. After being dried and crushed to fine powder, it was calcined at 850 °C for 10 h in air to obtain K₂Ti₂O₅. Co/K_xTi₂O₅ was prepared by introducing 2 g K₂Ti₂O₅ powder into 200 ml aqueous solution of Co(NO₃)₂ (Junsei Chemical Co., Ltd.). After the solution was kept stirring for a certain time, it was filtered and dried and this was followed by calcination at 500 °C for 5 h in air. By controlling the exchange time and the concentration of the Co precursor solution, we could get catalysts having different amount of K and Co loading.

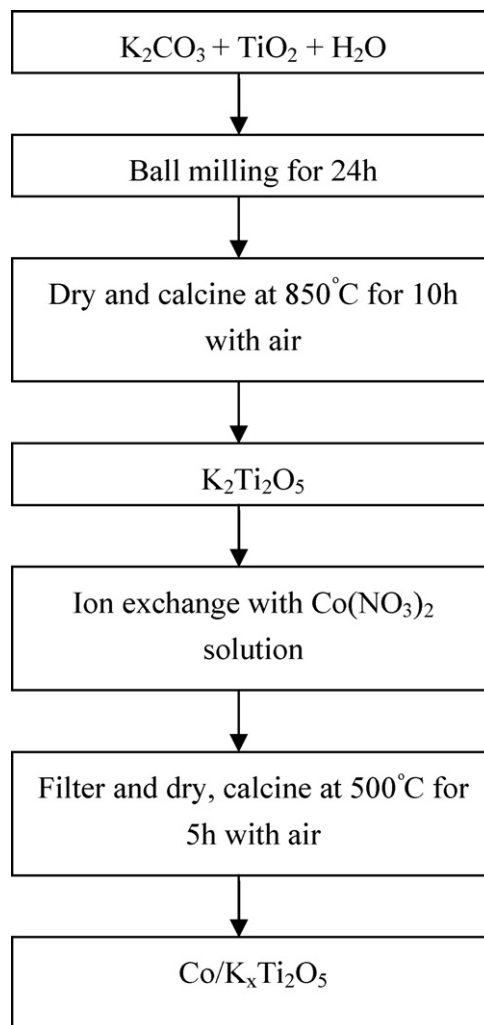


Fig. 1. Procedure of preparing Co/K_xTi₂O₅.

For comparison purpose, 20 wt.%Co/TiO₂ and 5 wt.%Co/TiO₂ catalysts were prepared by impregnation method. Co(NO₃)₂ (Junsei Chemical Co., Ltd.) solution was added to TiO₂ powder (Hombikat UV 100) drop by drop to the incipient wetness. 5 wt.%Co-1 wt.%K/TiO₂ catalysts were also synthesized with different kinds of K precursors, including potassium carbonate (Yakuri Pure Chemical Co., Ltd.), potassium nitrate (Shinyo pure chemicals CO., Ltd.) and potassium acetate (Sigma-Aldrich, 99 + % A.C.S reagents) by the same impregnation method. They were then dried at 105 °C over night and calcined at 500 °C for 5 h in air. All catalysts in present work were calcined using a box furnace in a static air environment.

2.2. Catalyst characterization

The compositions of the Co/K_xTi₂O₅ catalysts were examined by atomic absorption analysis (Model Spectra AA 800). BET surface area were obtained by measuring the amount of adsorbed N₂ at liquid N₂ temperature by means of Micromeritics ASAP 2010 sorption analyzer. The samples

Table 1

Compositions of K, Ti and Co, ion exchange parameters and surface areas of $K_2Ti_2O_5$, $Co/K_xTi_2O_5-1$ and $Co/K_xTi_2O_5-2$

Catalyst name	$Co(NO_3)_2$ (mol/l)	pH	Ion exchange time (h)	Co (wt.%)	K (wt.%)	Ti (wt.%)	K exchange level (%)	BET (m^2/g)
$K_2Ti_2O_5$	–	–	–	0	30.73	37.74	0	0.13
$Co/K_xTi_2O_5-1$	0.03	5.8	0.15	19.17	15.28	37.31	50.28	19.11
$Co/K_xTi_2O_5-2$	0.25	3.8	60	20.89	2.15	34.48	93.00	22.79

were degassed at 200 °C in vacuum for 5 h before absorption measurement. X-ray diffraction patterns were obtained using a X-ray analyzer (XRD, M18XHF, Mac Science Co., Japan). Ni-filtered Cu K α radiation ($\lambda = 1.5415 \text{ \AA}$) was used with an X-ray gun operated at 40 kV and 200 mA. Diffraction patterns were obtained within the range of $2\theta = 10\text{--}80^\circ$ with a step size of 0.02° . XPS analysis was performed with a VG Scientific ESCALAB 220-IXL using non-monochromated Mg K α radiation (1253.6 eV). The binding energy was corrected using a reference of the contaminated carbon (284.6 eV).

FT-IR experiments were performed by using a Perkin-Elmer 1800 FT-IR spectrophotometer. A self-supporting thin disc of 13 mm in diameter was prepared by pressing 15 mg catalyst powder using a manual hydraulic press. All spectra were measured with 4 cm^{-1} resolution. The temperature was measured with a thermocouple which was in contact with the grid. The sample was first exposed to 1000 ppm NO and 10% O_2 in He (flow rate 200 ml/min) at room temperature 30 min. After switched to a He flow (200 ml/min), it was heated up to 400 °C with a ramp of $10^\circ\text{C}/\text{min}$ and in situ spectra were recorded at desired temperatures. A reference spectrum was taken in a flow of He with the catalyst disc that did not experience NO and O_2 .

2.3. Reaction tests

Reaction tests were performed in a flow-reactor equipment, consisting of a packed bed made of quartz tube (10 mm internal diameter) in which 0.6 g powdered catalyst (bed depth = about 9 mm) was charged. The reactor was introduced into an electric furnace controlled by a PID temperature controller (Han Kook electronic Co.). The temperature of the catalyst was controlled by using a K-type thermocouple (outer diameter 0.5 mm) which was placed 1 mm above catalyst bed. The feed gas was composed of 700 ppm of NO and 0.4–10% O_2 in balanced He. The influence of NO concentration ranging from 100 ppm to 1500 ppm was tested with 5% O_2 . Flow rate of the feed was varied with space velocities ranging from $20,000 \text{ h}^{-1}$ to $240,000 \text{ h}^{-1}$. The exit gas was continuously analyzed by means of a NO_x analyzer (Chemiluminescence $NO\text{--}NO_2\text{--}NO_x$ analyzer, Model 42C, Thermo environmental instruments Inc.). The detection limit was 0.05 ppm for NO_x .

Catalyst deactivation by SO_2 was tested using SO_2 ranging from 8 ppm to 16 ppm in 700 ppm NO and 10% O_2 . NO_2 influence on the catalyst deactivation was also tested as follows: pre-treating catalyst in 550 ppm NO_2 and 10% O_2 at 250 °C for 2 h, then testing its activity in 700 ppm NO and 10% O_2 as a function of temperature.

3. Results and discussion

3.1. Catalyst characterization

By changing the concentration of $Co(NO_3)_2$ (as shown in Table 1) and the ion exchanging, two catalysts having similar cobalt loading but different amount of K were prepared and they were named as $Co/K_xTi_2O_5-1$ and $Co/K_xTi_2O_5-2$. Their exact contents of Co, K and Ti were analyzed by means of atomic absorption analysis. It was found that $Co/K_xTi_2O_5-1$ contains 15.28 wt.% of K, while $Co/K_xTi_2O_5-2$ contains only 2.15 wt.% of K. The exchange degree of K ion was 50.28% for $Co/K_xTi_2O_5-1$ and 93.00% for $Co/K_xTi_2O_5-2$. BET surface areas were also listed in Table 1.

Fig. 2 shows XRD patterns of $K_2Ti_2O_5$, $Co/K_xTi_2O_5-1$ and $Co/K_xTi_2O_5-2$. Synthesized $K_2Ti_2O_5$ has a good consistency with calculated diffraction patterns. SEM image shows a plate like structure for both $K_2Ti_2O_5$, $Co/K_xTi_2O_5-1$ (not shown here). After ion exchange, the regular patterns of the X-ray peak disappear indicating a collapse in the structure. $Co/K_xTi_2O_5-1$ showed less degree of structural collapse with some weak peaks of $K_2Ti_2O_5$ still remaining. However, for $Co/K_xTi_2O_5-2$ with longer ion exchange time and higher $Co(NO_3)_2$ concentration, majority of K (93%) was exchanged out and finally $K_2Ti_2O_5$ structure was converted to TiO_2 . Co_3O_4 peaks were found in XRD patterns of both $Co/K_xTi_2O_5-1$ and $Co/K_xTi_2O_5-2$. We therefore conclude that $Co/K_xTi_2O_5-1$ is composed of Co_3O_4 supported on K-rich amorphous like phase of $K_2Ti_2O_5$ and $Co/K_xTi_2O_5-2$ is Co_3O_4 supported on anatase TiO_2 . There is about 150 times increase in the BET surface area after the ion exchange.

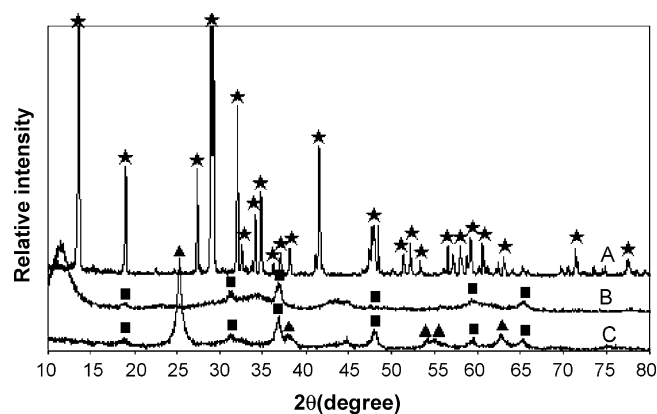


Fig. 2. XRD patterns of $K_2Ti_2O_5$ and $Co/K_xTi_2O_5-1$ and $Co/K_xTi_2O_5-2$. (★) $K_2Ti_2O_5$; (■) Co_3O_4 ; (▲) anatase TiO_2 .

3.2. Influence of GHSV

Fig. 3 shows the oxidation of 700 ppm NO at various GHSV values as a function of temperature with 10% O₂ in the feed. With increased GHSV from 20,000 h⁻¹ to 240,000 h⁻¹, the peak temperature at which the conversion becomes maximum is shifted to higher temperature (from 282 °C to 320 °C) and the maximum NO conversion decreases from 84.5% to 72%, which is due to the thermodynamic equilibrium given in Eq. (1).



In the kinetically controlled region (200–282 °C), the conversion decreases with increased GHSV. For example, at 250 °C the conversion is 51% for 20,000 h⁻¹ GHSV, but only 17% for 240,000 h⁻¹ GHSV. In the thermodynamically controlled region, the conversion is not influenced by GHSV and more or less falls on the theoretical line of the thermodynamic equilibrium within an error margin of ±5%.

3.3. Influence of O₂ concentration

The effect of O₂ concentration on the NO (700 ppm) oxidation is shown as a function of temperature in Fig. 4. The results show that the peak temperature decreases with a decrease in the O₂ concentration and decreases sharply as O₂ concentration approaches below 1%. The equilibrium conversion at high temperatures is also decreased with decreased O₂ concentration, and decreased sharply as O₂ concentration approaches below 1%. Below the peak temperature where the reaction is controlled kinetically, the conversion increases sharply with increasing temperature at high-oxygen concentration whereas the conversion increases only moderately with temperature at low-oxygen concentration. The same phenomenon was also observed for Pt-based catalysts by Després et al. [10].

3.4. Influence of NO concentration

The effect of NO concentration is also observed with 5% O₂ in feed, as shown in Fig. 5. Unlike oxygen effect, NO has a

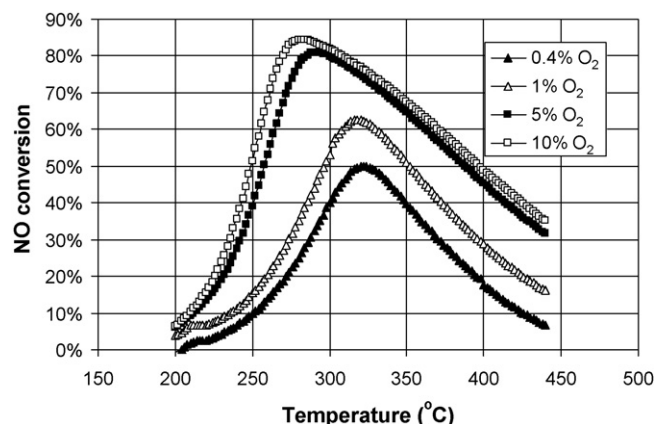


Fig. 4. Influence of the O₂ concentration on NO conversion as a function of temperature. Feed 700 ppm NO, 0.4–10% O₂ in He; temperature 200–440 °C; GHSV 20,000 h⁻¹.

negative effect on the reaction rate showing a decrease in the conversion with increased NO concentration. Thus, the peak temperature is shifted to higher temperature with increased NO concentration, for example, from 275 °C with 100 ppm NO to 325 °C with 1500 ppm NO. Above the peak temperature, the decreasing rate of NO conversion is almost the same for all the concentrations of NO due to thermodynamic equilibrium.

From the results in Figs. 4 and 5, we confirm the peak temperature is as low as that of Pt-based catalyst reported by Després et al. [10]. The high-catalytic activity of present catalyst may be due to the existence of Co oxides which have high-oxidative capacity or Co species combined with K atoms remaining in the catalyst after the ion exchange. It has been well known that the activity of cobalt oxide can be enhanced by the presence of K [22,28,29]. Therefore, it is imperative to investigate the effect of K on the NO oxidation.

3.5. The active species

XPS measurements were performed to find out the active species of our catalyst. Fig. 6 shows the XPS spectra of Co/

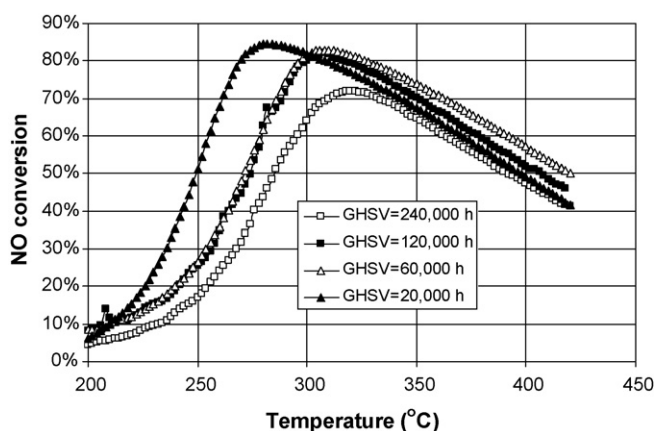


Fig. 3. Influence of GHSV on the conversion of NO as a function of temperature. Feed: 700 ppm NO, 10% O₂ in He; temperature 200–420 °C; GHSV 20,000–240,000 h⁻¹.

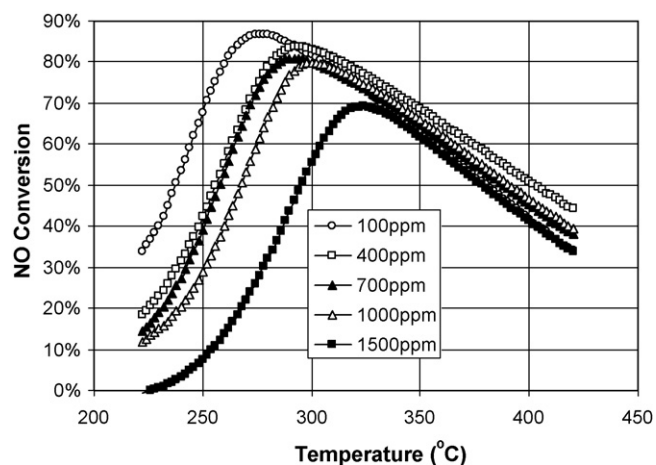


Fig. 5. Influence of the NO concentration on NO conversion as a function of temperature. Feed 100–1500 ppm NO, 5% O₂ in He; temperature 220–420 °C; GHSV: 20,000 h⁻¹.

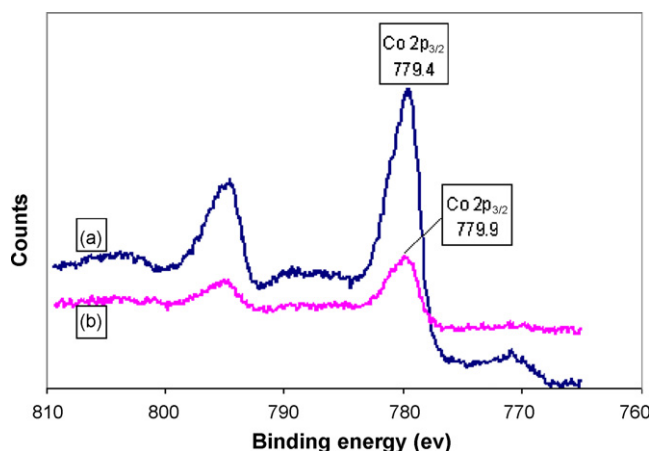


Fig. 6. XPS spectra of $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1 and 20 wt.% Co/TiO_2 . (a) $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1 and (b) Co/TiO_2 .

$\text{K}_x\text{Ti}_2\text{O}_5$ and impregnated Co/TiO_2 in the Co 2p region. The peaks of the Co $2p_{3/2}$ binding energy (BE) for both samples were appeared around 779.4–779.8 eV, which is in good agreement with the reference data for cobalt oxide, including CoO , Co_2O_3 and Co_3O_4 . However, either the absolute binding energy or the line separation between Co $2p_{1/2}$ and Co $2p_{3/2}$ is not a direct measure of the chemical state of Co species. Normally, there is a satellite peak on the high-binding energy side of the principal Co $2p_{1/2}$ and Co $2p_{3/2}$ that is believed to be characteristics of Co^{2+} [34,35]. In Fig. 6, we cannot find any satellite peak on the high-binding energy side of the principal Co $2p_{1/2}$ and Co $2p_{3/2}$, and can conclude that the Co species is not CoO . According to literature, cobaltic oxide (Co_2O_3) could be formed when cobalt compounds are heated at a low temperature in the presence of excess air. It can be completely converted into Co_3O_4 at temperatures higher than 538 K. Co_2O_3 absorbs oxygen and transforms to a higher oxide of Co_3O_4 , with no change in the lattice structure [36]. Based on these two points, we must conclude that the active Co species is Co_3O_4 , which was also observed by Vijay and co-workers [38,39].

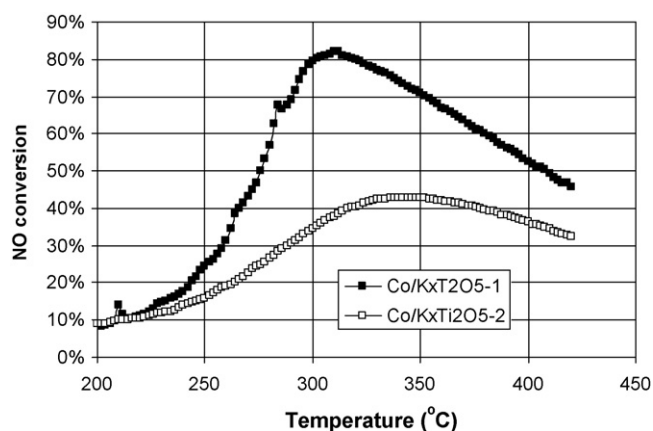


Fig. 7. NO conversions over $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1 and $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -2 as a function of temperature. Feed 700 ppm NO, 10% O_2 in He; temperature 200–420 °C; GHSV 120,000 h^{-1} .

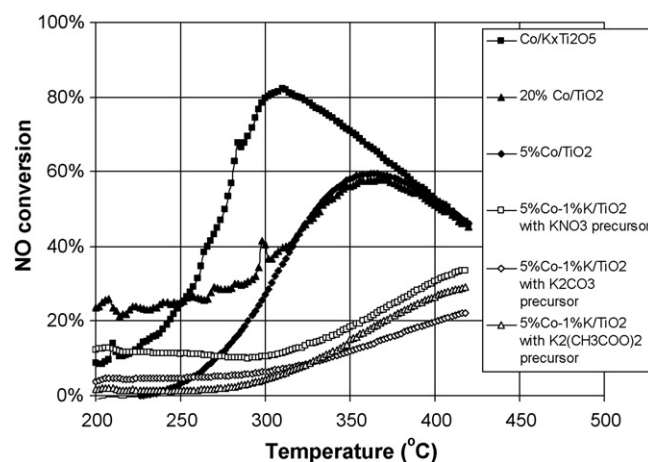


Fig. 8. NO conversions as a function of temperature on $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1, 20 wt.% Co/TiO_2 , 5 wt.% Co/TiO_2 , and 5 wt.% Co -1 wt.% K/TiO_2 made with different K precursors. Feed 700 ppm NO, 10% O_2 in He; temperature 200–420 °C; GHSV 120,000 h^{-1} .

Fig. 7 shows the NO conversions for $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1 and $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -2. Their activities are quite different even though the Co loading is almost same. $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1 shows 82% of NO to NO_2 conversion at a relatively low temperature (310 °C), whereas $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -2 having anatase TiO_2 structure shows much lower NO oxidation activity. Its maximum NO conversion is only 42% and the peak temperature is also high (340 °C). This data shows that NO oxidation activity is not only depended on Co_3O_4 , but also promoted by potassium remaining in $\text{K}_x\text{Ti}_2\text{O}_5$ support.

3.6. Effect of $\text{K}_2\text{Ti}_2\text{O}_5$ support

Comparing the XPS spectra of $\text{Co/K}_x\text{Ti}_2\text{O}_5$ and impregnated Co/TiO_2 in Fig. 6, the addition of K causes a slight shift in the binding energy for Co $2p_{3/2}$ level to a lower value (from 779.8 eV to 779.4 eV), suggesting a change in the electronic state of the cobalt. Haneda also found the same results with K doped cobalt oxides [37]. In order to understand the effect of K on the NO oxidation, we prepared 20 wt.% Co/TiO_2 , 5 wt.% Co/TiO_2 , and 5 wt.% Co -1 wt.% K/TiO_2 catalysts with three different potassium precursors and their catalytic activities for the NO oxidation were tested at the same condition as $\text{Co/K}_x\text{Ti}_2\text{O}_5$ catalysts. Fig. 8 shows that the maximum NO conversion of $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1 (around 82%) is much higher than those of 20 wt.% Co/TiO_2 and 5 wt.% Co/TiO_2 (less than 60%), and the peak temperature of $\text{Co/K}_x\text{Ti}_2\text{O}_5$ -1 (around 310 °C) is much lower than those of 20 wt.% Co/TiO_2 and 5 wt.% Co/TiO_2 (around 360 °C). When K was introduced to 5 wt.% Co/TiO_2 directly by impregnation method, however, we could not observe any improvement in the NO oxidation activity. NO conversions of all of the 5 wt.% Co -1 wt.% K/TiO_2 catalysts with three different potassium precursors are even worse than 5 wt.% Co/TiO_2 without K. The results are different from those obtained with Pt-based catalysts. Mulla et al. [22] reported that potassium-added Pt-K/ Al_2O_3 has lower apparent activation energy (60 kJ mol^{-1}) than that of Pt/ Al_2O_3 catalyst (82 kJ mol^{-1}).

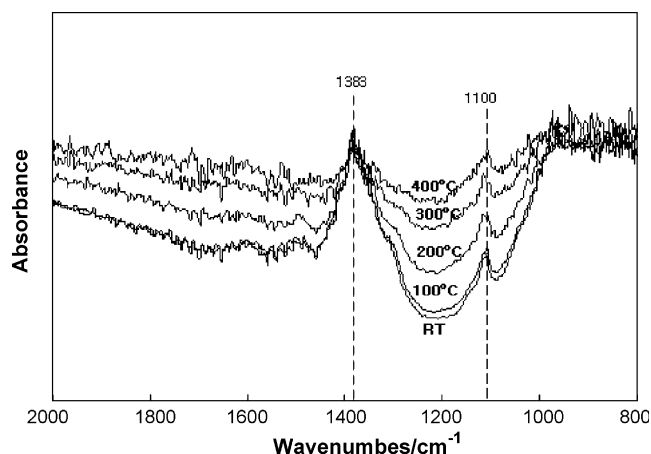


Fig. 9. FT-IR spectra of pretreated $\text{Co/K}_x\text{Ti}_2\text{O}_5$ catalyst recorded at different temperatures (RT, 100 °C, 200 °C, 300 °C and 400 °C) in He.

3.7. Surface transient species

NO_x chemisorbed on catalyst surface was investigated by FT-IR and the results are shown in Fig. 9. Two types of adsorbed NO_x species were formed: free ionic nitrate (1383 cm^{-1} , NO_3^-) and bridged nitrate (1100 cm^{-1}) species [28,40]. According to Toops's report, the dominant nitrate species at 1383 cm^{-1} is associated with potassium [40]. With increased temperature, intensities of both transient species are decreased, especially the ionic nitrate at 1383 cm^{-1} . These formed transient NO_x species shows that $\text{Co/K}_x\text{Ti}_2\text{O}_5$ catalyst plays a critical role for NO oxidation.

4. Catalyst deactivation

4.1. SO_2 poisoning

SO_2 poisoning is one of the key problems for Pt-based catalysts. Xue et al. [17,21] reported that, in the presence of SO_2 , the catalytic activity of the NO oxidation dropped dramatically with Pt-based catalysts ($\text{Pt}/\gamma\text{-Al}_2\text{O}_3$, Pt/SiO_2 and Pt/ZrO_2). TiO_2 is known to be more resistant to sulfur poisoning. Takeuchi and Masahiko [33] reported that titanium oxide (TiO_2) is the most promising candidate for the support to overcome sulfur poisoning. The stability of sulfate on the TiO_2 surface is weaker than that on other oxides [31,32]. Expecting similar properties of $\text{K}_2\text{Ti}_2\text{O}_5$ to TiO_2 concerning sulfur resistant, this aspect was evaluated using an accelerated deactivation test with SO_2 whose concentration was one order

Table 2
Maximum EU-allowed sulfur concentration in exhaust gases and fuels [1]

EU dead line	Concentration of SO_2 in exhaust gases (vol. ppm)	Concentration of S in gasoline (mg/kg)	Concentration of S in diesel fuel (mg/kg)
01/01/2000	7.5	150	350
01/01/2005	2.5/0.5	50/10	50/10
01/01/2009	0.5	10	10

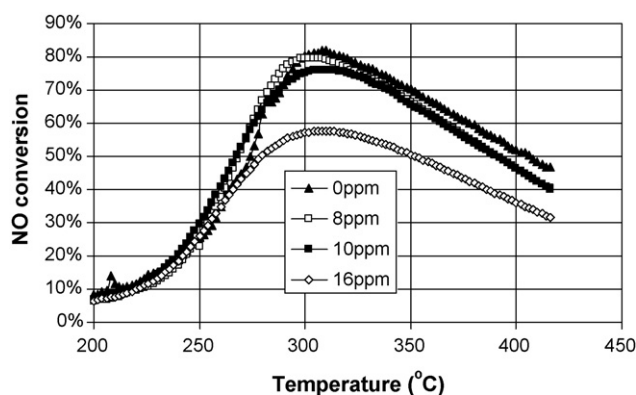


Fig. 10. Influence of SO_2 on NO conversion as a function of temperature. Feed 700 ppm NO, 10% O_2 in He; temperature 200–420 °C; GHSV 120,000 h^{-1} .

of magnitude higher than the typical value in gasoline engine emission, ranging from 8 ppm to 16 ppm [1]. The maximum European regulation allowed for sulfur concentration in exhaust gases and fuels is presented in Table 2. The results tested with $\text{Co/K}_x\text{Ti}_2\text{O}_5$ catalysts are shown in Fig. 10. When the SO_2 concentration is kept within 10 ppm, there is only a slight decrease in the NO conversion, which indicates that $\text{Co/K}_x\text{Ti}_2\text{O}_5$ is resistant to the SO_2 poisoning. While increasing SO_2 concentration to 16 ppm, the catalyst activity decreases appreciably.

4.2. NO_2 inhibition

For Pt-based catalyst, the active catalytic site for NO oxidation is reduced form of Pt, not Pt oxides (PtO , PtO_2). In the presence of NO_2 , which is a product of the reaction, Pt will be oxidized to Pt oxides, leading to the deactivation of Pt-based catalyst [10,19]. Because of such inevitable influence of NO_2 , Pt is not a promising catalyst for NO oxidation. For $\text{Co/K}_x\text{Ti}_2\text{O}_5$, the active species is Co oxides, which could be more resistant to NO_2 . Fig. 11 shows the oxidation of 700 ppm NO as a function of temperature over fresh catalyst and catalyst pretreated with 550 ppm NO_2 and 10% O_2 . The pretreated

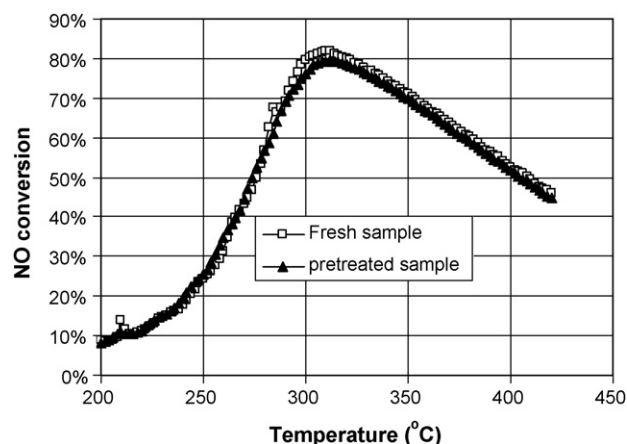


Fig. 11. Oxidation of NO over fresh and NO_2 -pretreated catalysts. Feed 700 ppm NO, 10% O_2 in He; temperature 200–420 °C; GHSV: 120,000 h^{-1} .

catalyst shows the same activity as fresh one, which establishes that NO₂ has no negative effect on the catalytic activity of Co/K_xTi₂O₅. Després et al. [10] did the same experiment over Pt-based catalyst. The activity of the pretreated catalyst was much lower than that of fresh catalyst. The conversion of NO to NO₂ decreased from around 80% to 70%.

5. Conclusion

K₂Ti₂O₅ was synthesized and Co/K_xTi₂O₅ catalysts were prepared by ion exchange method. In order to see the effect of K, two different catalysts of Co/K_xTi₂O₅ having the same Co loading but different K content can be prepared by changing concentration of Co precursor and ion exchange time.

The prepared catalysts were tested for NO oxidation, and their activities were compared with Co doped on TiO₂ or K/TiO₂. Investigation on the influence of GHSV, O₂ concentration and NO concentration on the NO conversion established that activity of K-rich Co/K_xTi₂O₅ catalyst is superior to those of Co/TiO₂ or Co-K/TiO₂ and similar to those of Pt-based catalysts. The peak temperature at a maximum NO conversion depends strongly on GHSV, O₂ and NO. Increasing O₂ concentration up to 10%, the peak temperature for oxidizing 700 ppm NO can be decreased down to 282 °C. Decreasing NO concentration down to 100 ppm can decrease the peak temperature down to 276 °C even with 5% O₂ in feed. The peak temperature is as low as that with Pt-based catalyst.

Promotional effect of cobalt oxides (Co₃O₄) with K remaining in K₂Ti₂O₅ support is the reason of high-catalytic activity. FT-IR analysis confirmed the existence of chemisorbed species of NO_x formed on the surface of Co/K_xTi₂O₅ catalysts.

Deactivation tests have shown that Co/K_xTi₂O₅ catalyst is resistant to SO₂. There is negligible decrease in the NO conversion if SO₂ concentration is kept less than 10 ppm. Unlike Pt-based catalysts, NO₂ also has no inhibition effect in the NO oxidation.

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